WHAT IS CLAIMED AS NEW AND IS DESIRED TO BE SECURED BY LETTERS PATENT OF THE UNITED STATES IS:

1. A process of atom or group transfer radical polymerization, comprising the steps of:

polymerizing one or more radically polymerizable monomers in the presence of an initiator having a radically transferable atom or group, a transition metal compound and a ligand to form a (co)polymer, the transition metal compound being capable of participating in a redox cycle with the initiator and a dormant polymer chain, and the ligand being any N-, O-, P- or S- containing compound which can coordinate in a σ-bond to the transition metal or any carbon-containing compound which can coordinate in a π-bond to the transition metal, such that direct bonds between the transition metal and growing polymer radicals are not formed, and

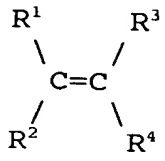
isolating the formed (co)polymer.

2. The process of Claim 1, wherein the amounts of said monomer(s), said initiator, said transition metal compound and said ligand are such that growing radicals are present during said polymerizing in a concentration in the range of from 10^{-9} mol/L to 10^{-6} mol/L, and dormant polymer chains are present during said polymerizing in a concentration in the range of from 10^{-4} mol/L to 1 mol/L.

3. The process of Claim 2, wherein the concentration of said growing radicals is from 10^{-8} mol/L to 10^{-6} mol/L.

4. The process of Claim 2, wherein the concentration of said dormant polymer chains is from 10^{-4} mol/L to 1 mol/L.

5. The process of Claim 1, wherein said monomer(s) are of the formula:



wherein R^1 and R^2 are independently selected from the group consisting of H, halogen, CN, CF_3, straight or branched alkyl of from 1 to 20 carbon atoms, α,β-unsaturated straight or branched alkenyl or alkynyl of 2 to 10 carbon atoms, α,β-unsaturated straight or branched alkenyl of 2 to 6 carbon atoms substituted with a halogen, C_3-C_8 cycloalkyl, heterocyclyl, $C(=Y)R^5$, $C(=Y)NR^6R^7$ and $YC(=Y)R^8$; where Y may be NR^8 or O; R^5 is alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy; R^6 and R^7 are independently H or alkyl of from 1 to 20 carbon atoms, or R^6 and R^7 may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring; and R^8 is H, straight or branched C_1-C_{20} alkyl or aryl; and

R^3 and R^4 are independently selected from the group consisting of H, halogen, C_1-C_6 alkyl and $COOR^9$, where R^9 is H, an alkali metal, or a C_1-C_6 alkyl group; or

R^1 and R^3 may be joined to form a group of the formula $(CH_2)_{n'}$ or a group of the formula C(=O)-Y-C(=O), where n' is from 2 to 6, the group $(CH_2)_{n'}$ may be substituted with from 1 to 2n' halogen atoms or C_1-C_4 alkyl groups, and Y is as defined above; and

at least two of R^1, R^2, R^3 and R^4 are H or halogen.

6. The process of Claim 1, wherein said initiators is of the formula:

$$R^{11}R^{12}R^{13}C\text{-}X$$

where:

X is selected from the group consisting of Cl, Br, I, OR^{10}, SR^{14}, SeR^{14}, $OP(=O)R^{14}$, $OP(=O)(OR^{14})_2$, $OP(=O)OR^{14}$, $O\text{-}N(R^{14})_2$ and $S\text{-}C(=S)N(R^{14})_2$, where R^{10} is alkyl of from 1 to 20 carbon atoms in which each of the hydrogen atoms may be independently replaced by halide, R^{14} is aryl or a straight or branched C_1-C_{20} alkyl group, and where an $N(R^{14})_2$ group is present, the two R^{14} groups may be joined to form a 5- or 6-membered heterocyclic ring; and

R^{11}, R^{12} and R^{13} are each independently selected from the group consisting of H, halogen, C_1-C_{20} alkyl, C_3-C_8 cycloalkyl, $C(=Y)R^5$, $C(=Y)NR^6R^7$, COCl, OH, CN, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl oxiranyl, glycidyl, aryl, heterocyclyl, aralkyl, aralkenyl, C_1-C_6 alkyl in which from 1 to all of the hydrogen atoms are

replaced with halogen and C_1-C_6 alkyl substituted with from 1 to 3 substituents selected from the group consisting of C_1-C_4 alkoxy, aryl, heterocyclyl, $C(=Y)R^5$, $C(=Y)NR^6R^7$, oxiranyl and glycidyl;

where R^5 is alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy; and R^6 and R^7 are independently H or alkyl of from 1 to 20 carbon atoms, or R^6 and R^7 may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring;

such that no more than two of R^{11}, R^{12} and R^{13} are H.

7. The process of Claim 6, wherein no more than one of R^{11}, R^{12} and R^{13} is H.

8. The process of Claim 1, wherein said transition metal compound is of the formula $M_t^{n+}X'_n$, where:

M_t^{n+} may be selected from the group consisting of Cu^{1+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Ru^{2+}, Ru^{3+}, Cr^{2+}, Cr^{3+}, Mo^{2+}, Mo^{3+}, W^{2+}, W^{3+}, Mn^{3+}, Mn^{4+}, Rh^{3+}, Rh^{4+}, Re^{2+}, Re^{3+}, Co^{+}, Co^{2+}, V^{2+}, V^{3+}, Zn^{+}, Zn^{2+}, Au^{+}, Au^{2+}, Ag^{+} and Ag^{2+};

X' is selected from the group consisting of halogen, C_1-C_6-alkoxy, $(SO_4)_{1/2}$, $(PO_4)_{1/3}$, $(R^{14}PO_4)_{1/2}$, $(R^{14}{}_2PO_4)$, triflate, hexafluorophosphate, methanesulfonate, arylsulfonate, CN and $R^{15}CO_2$, where R^{15} is H or a straight or branched C_1-C_6 alkyl

group which may be substituted from 1 to 5 times with a halogen; and

n is the formal charge on the metal ($0 \leq n \leq 7$).

9. The process of Claim 1, wherein said ligand is selected from the group consisting of:

compounds of the formulas:

$$R^{16}-Z-R^{17}$$

$$R^{16}-Z-(R^{18}-Z)_m-R^{17}$$

where:

R^{16} and R^{17} are independently selected from the group consisting of H, C_1-C_{20} alkyl, aryl, heterocyclyl and C_1-C_6 alkyl substituted with C_1-C_6 alkoxy, C_1-C_4 dialkylamino, $C(=Y)R^5$, $C(=Y)R^6R^7$ and $YC(=Y)R^8$, where Y may be NR^8 or O; R^5 is alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy; R^6 and R^7 are independently H or alkyl of from 1 to 20 carbon atoms, or R^6 and R^7 may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring; and R^8 is H, straight or branched C_1-C_{20} alkyl or aryl;

Z is O, S, NR^{19} or PR^{19}, where R^{19} is selected from the same group as R^{16} and R^{17}, and where Z is PR^{19}, R^{19} can also be C_1-C_{20}-alkoxy;

each R^{18} is independently a divalent group selected from the group consisting of C_3-C_8 cycloalkanediyl, C_3-C_8

cycloalkenediyl, arenediyl and heterocyclylene where the covalent bonds to each Z are at vicinal positions, and C_2-C_4 alkylene and C_2-C_4 alkenylene where the covalent bonds to each Z are at vicinal positions or at β-positions; and

m is from 1 to 6;

compounds of the above formulas where R^{16} and R^{17} can be joined to form a saturated, unsaturated or heterocyclic ring;

compounds of the above formulas where each of R^{16}-Z and R^{17}-Z form a ring with the R^{18} group to which the Z is bound to form a linked or fused heterocyclic ring system;

compounds of the above formulas where one or both of R^{16} and R^{17} are heterocyclyl, and in which Z is a covalent bond, CH_2 or a 4- to 7-membered ring fused to R^{16} or R^{17} or both;

CO;

porphyrins and porphycenes, which may be substituted with from 1 to 6 halogen atoms, C_1-C_6 alkyl groups, C_1-C_6-alkoxy groups, C_1-C_6 alkoxycarbonyl, aryl groups, heterocyclyl groups, and C_1-C_6 alkyl groups further substituted with from 1 to 3 halogens;

compounds of the formula $R^{20}R^{21}C(C(=Y)R^5)_2$, where Y and R^5 are as defined above, and each of R^{20} and R^{21} is independently selected from the group consisting of H, halogen, C_1-C_{20} alkyl, aryl and heterocyclyl, and R^{20} and R^{21} may be joined to form a C_3-C_8 cycloalkyl ring or a hydrogenated aromatic or heterocyclic ring, any of which (except for H and halogen) may be further substituted with 1 to 5 C_1-C_6 alkyl groups, C_1-C_6

alkoxy groups, halogen atoms, aryl groups, or combinations thereof; and

arenes and cyclopentadienyl ligands, where said cyclopentadienyl ligand may be substituted with from one to five methyl groups, or may be linked through an ethylene or propylene chain to a second cyclopentadienyl ligand.

10. The process of Claim 1, wherein the initiator is present in a concentration of from 10^{-4} M to 1 M.

11. The process of Claim 1, wherein the initiator and monomer(s) are present in amounts providing a molar ratio of from 10^{-4}:1 to 10^{-1}:1 of initiator to monomer(s).

12. The process of Claim 1, wherein the transition metal compound is present in an amount providing a molar ratio of transition metal compound to initiator of from 0.001:1 to 10:1.

13. The process of Claim 1, wherein the ligand is present in an amount providing a ratio of (a) coordination sites on the transition metal compound to (b) coordination sites which the ligand will occupy of from 0.1:1 to 100:1.

14. The process of Claim 1, wherein the monomer, initiator, transition metal compound and ligand are selected

such that (a) the rate of initiation in said polymerizing step is not less than 1,000 times slower than (b) the rate of propagation in said polymerizing step or of transfer of the radically transferable group to the polymer radical.

15. A copolymer of the formula:

$$R^{11}R^{12}R^{13}C-(M^1)_p-(M^2)_q-X$$

$$R^{11}R^{12}R^{13}C-(M^1)_p-(M^2)_q-(M^3)_r-X$$

$$R^{11}R^{12}R^{13}C-(M^1)_p-(M^2)_q-(M^3)_r-\ldots-(M^u)_s-X$$

wherein X is selected from the group consisting of Cl, Br, I, OR^{10}, SR^{14}, SeR^{14}, $O-N(R^{14})_2$, $S-C(=S)N(R^{14})_2$, H, OH, N_3, NH_2, COOH and $CONH_2$, where

R^{10} is alkyl of from 1 to 20 carbon atoms in which each of the hydrogen atoms may be independently replaced by halide, R^{14} is aryl or a straight or branched C_1-C_{20} alkyl group, and where an $N(R^{14})_2$ group is present, the two R^{14} groups may be joined to form a 5- or 6-membered heterocyclic ring,

R^{11}, R^{12} and R^{13} are each independently selected from the group consisting of H, halogen, C_1-C_{20} alkyl, C_3-C_8 cycloalkyl, $C(=Y)R^5$, $C(=Y)NR^6R^7$, COCl, OH, CN, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl oxiranyl, glycidyl, aryl, heterocyclyl, aralkyl, aralkenyl, C_1-C_6 alkyl in which from 1 to all of the hydrogen atoms are replaced with halogen and C_1-C_6 alkyl substituted

with from 1 to 3 substituents selected from the group consisting of C_1-C_4 alkoxy, aryl, heterocyclyl, $C(=Y)R^5$, $C(=Y)NR^6R^7$, oxiranyl and glycidyl, where

R^5 is alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy; and R^6 and R^7 are independently H or alkyl of from 1 to 20 carbon atoms, or R^6 and R^7 may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring,

such that no more than two of R^{11}, R^{12} and R^{13} are H, and

M^1, M^2, M^3,... up to M^u are each a radically polymerizable monomer selected such that the monomers in adjacent blocks are not identical, and p, q, r,... up to s are independently selected such that the number average molecular weight of each block is from 1,000 to 250,000 g/mol;

the following formulas:

$$X-(M^2)_q-(M^1)_p-(R^{11}R^{12}R^{13}C)-(M^1)_p-(M^2)_q-X$$

$$X-(M^3)_r-(M^2)_q-(M^1)_p-(R^{11}R^{12}R^{13}C)-(M^1)_p-(M^2)_q-(M^3)_r-X$$

$$X-(M^u)_s-\ldots-(M^3)_r-(M^2)_q-(M^1)_p-(R^{11}R^{12}R^{13}C-(M^1)_p-(M^2)_q-(M^3)_r-\ldots-(M^u)_s-X$$

wherein R^{11}, R^{12}, R^{13}, X, M^1, M^2, M^3,... up to M^u, and p, q, r,... up to s are as defined above;

of the formulas:

$$R^{11}R^{12}R^{13}C-(M^1-M^2)_p-(M^2-M^1)_q-(M^1-M^2)_r-\ldots-(M^v-M^y)_s-X$$

$$(R^{11}R^{12}R^{13}C)-[(M^1-M^2)_p-(M^2-M^1)_q-(M^1-M^2)_r-\ldots-(M^v-M^y)_s-X$$

where R^{11}, R^{12}, R^{13} and X are as defined above,

M^1 and M^2 are different radically-polymerizable monomers, and M^v is one of M^1 and M^2 and M^y is the other of M^1 and M^2, and

p, q, r,... up to s are independently selected such that the number average molecular weight of the copolymer is from 1,000 to 1,000,000 g/mol;

of the formulas:

$$(R^{11'}R^{12'}R^{13'}C)-[(M^1)_p-X]_z$$

$$(R^{11'}R^{12'}R^{13'}C)-[(M^1)_p-(M^2)_q-X]_z$$

$$(R^{11'}R^{12'}R^{13'}C)-[(M^1)_p-(M^2)_q-(M^3)_r-X]_z$$

$$(R^{11'}R^{12'}R^{13'}C)-[(M^1)_p-(M^2)_q-(M^3)_r-\ldots-(M^u)_s-X]_z$$

where $R^{11'}$, $R^{12'}$ and $R^{13'}$ are the same as R^{11}, R^{12} and R^{13} with the proviso that $R^{11'}$, $R^{12'}$ and $R^{13'}$ combined contain from 2 to 5 X groups, where X is as defined above;

M^1, M^2, M^3,... M^u are as defined above; and

z is from 3 to 6; and

of the formula:

$$^{R11}R^{12}R^{13}C-(M^1{}_aM^2{}_b)-(M^1{}_cM^2{}_d)-(M^1{}_eM^2{}_f)-\ldots-(M^1{}_gM^2{}_h)-(M^1{}_iM^2{}_j)-X$$

where R^{11}, R^{12}, R^{13} and X are as defined above, M^1 and M^2 are different radically-polymerizable monomers, and a, b, c, d, e, f,... up to g and h are non-negative numbers independently selected such that a + b = c + d = 100, and any or all of (e + f), (g + h) and (i + j) = 100 or 0, wherein the a:b ratio is from 100:0 to 0:100, the c:d ratio is from 95:5 to 5:95, such that c < a and d > b, and where applicable, the e:f ratio is from 90:10 to 10:90, such that e < c and f > d, and the endpoints of the molar ratio ranges of first monomer to second monomer in successive blocks progressively decrease or increase by 5 such that the e:f ratio is from 5:95 to 95:5, such that e ≠ c and f ≠ d, and the i:j ratio is from 0:100 to 100:0, such that i ≠ e and j ≠ f.

16. The copolymer of Claim 15, having a formula:

$$R^{11}R^{12}R^{13}C-(M^1)_p-(M^2)_q-X$$

$$R^{11}R^{12}R^{13}C-(M^1)_p-(M^2)_q-(M^3)_r-X \text{ or}$$

$$R^{11}R^{12}R^{13}C-(M^1)_p-(M^2)_q-(M^3)_r-\ldots-(M^u)_s-X$$

wherein X is selected from the group consisting of Cl, Br, I, OR^{10}, SR^{14}, SeR^{14}, $O-N(R^{14})_2$, $S-C(=S)N(R^{14})_2$, H, OH, N_3, NH_2, COOH and $CONH_2$; and where

R^{10} is alkyl of from 1 to 20 carbon atoms in which each of the hydrogen atoms may be independently replaced by halide, R^{14} is aryl or a straight or branched C_1-C_{20} alkyl

group, and where an $N(R^{14})_2$ group is present, the two R^{14} groups may be joined to form a 5- or 6-membered heterocyclic ring,

R^{11}, R^{12} and R^{13} are each independently selected from the group consisting of H, halogen, C_1-C_{20} alkyl, C_3-C_8 cycloalkyl, $C(=Y)R^5$, $C(=Y)NR^6R^7$, COCl, OH, CN, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl oxiranyl, glycidyl, aryl, heterocyclyl, aralkyl, aralkenyl, C_1-C_6 alkyl in which from 1 to all of the hydrogen atoms are replaced with halogen and C_1-C_6 alkyl substituted with from 1 to 3 substituents selected from the group consisting of C_1-C_4 alkoxy, aryl, heterocyclyl, $C(=Y)R^5$, $C(=Y)NR^6R^7$, oxiranyl and glycidyl, where

R^5 is alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy; and R^6 and R^7 are independently H or alkyl of from 1 to 20 carbon atoms, or R^6 and R^7 may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring,

such that no more than two of R^{11}, R^{12} and R^{13} are H, and

M^1, M^2, M^3,... up to M^u are each a radically polymerizable monomer selected such that the monomers in adjacent blocks are not identical, and p, q, r,... up to s are independently selected such that the number average molecular weight of each block is from 1,000 to 250,000 g/mol.

17. The copolymer of Claim 15, having a formula:

$$X-(M^2)_q-(M^1)_p-(R^{11}R^{12}R^{13}C)-(M^1)_p-(M^2)_q-X$$

$$X-(M^3)_r-(M^2)_q-(M^1)_p-(R^{11}R^{12}R^{13}C)-(M^1)_p-(M^2)_q-(M^3)_r-X \text{ or}$$

$$X-(M^u)_s-\ldots-(M^3)_r-(M^2)_q-(M^1)_p-(R^{11}R^{12}R^{13}C)-(M^1)_p-(M^2)_q-(M^3)_r-\ldots-(M^u)_s-X$$

wherein R^{11}, R^{12}, R^{13}, X, M^1, M^2, M^3,... up to M^u, and p, q, r,... up to s are as defined in Claim 15.

18. The copolymer of Claim 15, having a formula:

$$R^{11}R^{12}R^{13}C-(M^1-M^2)_p-(M^2-M^1)_q-(M^1-M^2)_r-\ldots-(M^v-M^y)_s-X \text{ or}$$

$$(R^{11}R^{12}R^{13}C)-[(M^1-M^2)_p-(M^2-M^1)_q-(M^1-M^2)_r-\ldots-(M^v-M^y)_s-X$$

where R^{11}, R^{12}, R^{13} and X are as defined in Claim 15, M^1 and M^2 are different radically-polymerizable monomers, and M^v is one of M^1 and M^2 and M^y is the other of M^1 and M^2, and

p, q, r,... up to s are independently selected such that the number average molecular weight of the copolymer is from 1,000 to 1,000,000 g/mol.

19. The copolymer of Claim 15, having a formula:

$$(R^{11'}R^{12'}R^{13'}C)-[(M^1)_p-X]_z$$

$$(R^{11'}R^{12'}R^{13'}C)-[(M^1)_p-(M^2)_q-X]_z$$

$$(R^{11'}R^{12'}R^{13'}C)-[(M^1)_p-(M^2)_q-(M^3)_r-X]_z \text{ or}$$

$$(R^{11'}R^{12'}R^{13'}C)-[(M^1)_p-(M^2)_q-(M^3)_r-\ldots-(M^u)_s-X]_z$$

where $R^{11'}$, $R^{12'}$ and $R^{13'}$ are the same as R^{11}, R^{12} and R^{13} as defined in Claim 15, with the proviso that $R^{11'}$, $R^{12'}$ and $R^{13'}$ combined contain from 2 to 5 X groups, where X is as defined above;

M^1, M^2, M^3,... M^u are as defined above; and

z is from 3 to 6.

20. The copolymer of Claim 15, having the formula:

$$R^{11}R^{12}R^{13}C-(M^1_aM^2_b)-(M^1_cM^2_d)-(M^1_eM^2_f)-\ldots-(M^1_gM^2_h)-(M^1_iM^2_j)-X$$

where R^{11}, R^{12}, R^{13} and X are as defined in Claim 15, M^1 and M^2 are different radically-polymerizable monomers, and a, b, c, d, e, f,... up to g and h are non-negative numbers independently selected such that a + b = c + d = 100, and any or all of (e + f), (g + h) and (i + j) = 100 or 0, wherein the a:b ratio is from 100:0 to 0:100, the c:d ratio is from 95:5 to 5:95, such that c < a and d > b, and where applicable, the e:f ratio is from 90:10 to 10:90, such that e < c and f > d, and the endpoints of the molar ratio ranges of first monomer to second monomer in successive blocks progressively decrease or increase by 5 such that the e:f ratio is from 5:95 to 95:5, such that e ≠ c and f ≠ d, and the i:j ratio is from 0:100 to 100:0, such that i ≠ e and j ≠ f.